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Towards in-situ biogas sensing

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Abstract

Among the renewable energy technologies, biogas plants are particularly interesting since they offer a reliable, steady source of electricity and heat. Both the composition as well as the quality of the biogas are crucial parameters for monitoring and optimizing the complete process chain. Currently employed systems only allow for ex-situ measurements using complex extraction machinery. Furthermore, due to their high cost a widespread use is prevented, especially in small biogas plants. To overcome these deficiencies and enable a continuous, reliable and precise determination of the gas composition innovative sensor systems are much needed. This contribution presents a novel in-situ approach capable of measuring the gas concentration of the most important biogas components continuously and in real time. This is achieved by using a combination of metal oxide based gas sensing and a photoacoustic detection scheme.

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Keywords: Multigas sensor system, Photoacoustics, Copper(II)oxide, Biogas monitoring, Chemosensing

1. Introduction

Biogas plants have been playing and will continue to play a pivotal role within the renewable energy sector. During the last two decades the importance of energy conversion from biomass through anaerobic digestion and the production of biogas has been growing steadily, accounting for about 10% of the global energy supply in 2013 [1]. The benefits of using biogas include its local production and use as heat and electricity source. However, quality control of biogas

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is oftentimes neglected due to the high cost associated with sensor equipment. Yet, to increase the efficiency and reduce the costs of biogas plants it is necessary to understand and monitor the ongoing processes in order to optimize the facilities accordingly [2].

Biogas is produced via an anaerobic digestion process resulting in a gas matrix mainly consisting of methane (CH_4) and carbon dioxide (CO_2) [3]. The most important by-product is the highly corrosive and toxic gas hydrogen sulfide (H_2S) which consequently has to be monitored as well. Currently employed technologies, namely so-called non-dispersive infrared spectrometers for methane and carbon dioxide and electro-chemical cells for hydrogen sulfide suffer from cross-sensitivities and long-term drifts, respectively [4, 5].

Here, a low-cost, in-situ system monitoring these gas with high precision would allow for new methods to operate biogas plants and increase their yield. For this reason the design presented here is composed of low-cost components with the possibility for complete integration into a single robust and reliable in-situ system.

2. Sensor conception

In order to achieve the selective, reliable, sensitive and cost-effective in-situ determination of CO_2 and CH_4 concentrations a photoacoustic based spectroscopy scheme is employed in the system. Unlike commonly employed setups a non-resonant, hermetically sealed chamber filled with the target gas is used to detect the infrared intensity of a modulated thermal source. This makes the use of optical filters unnecessary since the photoacoustic detector itself acts as wavelength selective element.

For the selective determination of the H_2S content in the gas matrix a novel concept to read-out copper(II)oxide (CuO) layers has been used [6]. It relies on determining the time necessary for the CuO layer to become electrically conductive upon H_2S exposure. The phase transition is reversible via a temperature procedure and is selective, i.e. only happens when applying H_2S. Since the determination of the target gas concentration is achieved by measuring a time, drifts in the sensor baseline are irrelevant.

Figure 1 depicts a schematic overview of the sensor system. A PSoC© 5LP [7] microcontroller is used to operate and read-out the individual system components. The temperature of the CuO layer is controlled via the current applied to a microintegrated tantalum/platinum meander and the electrical resistivity of the gas sensitive layer is read-out using an interdigitated electrode structure, as shown in Figure 2b [8]. To generate a photoacoustic signal inside the hermetically sealed micro-chamber which is schematically shown in Figure 2a, a planar thermal emitter is modulated with a sine-wave current at 20 Hz. The resulting sound wave is detected with a MEMS microphone and the signal is analyzed using the Goertzel-algorithm [9]. An I^2C temperature and humidity sensor from Honeywell [10] allows for the determination of the respective quantities and also to correct for small cross-sensitivities towards water vapor.

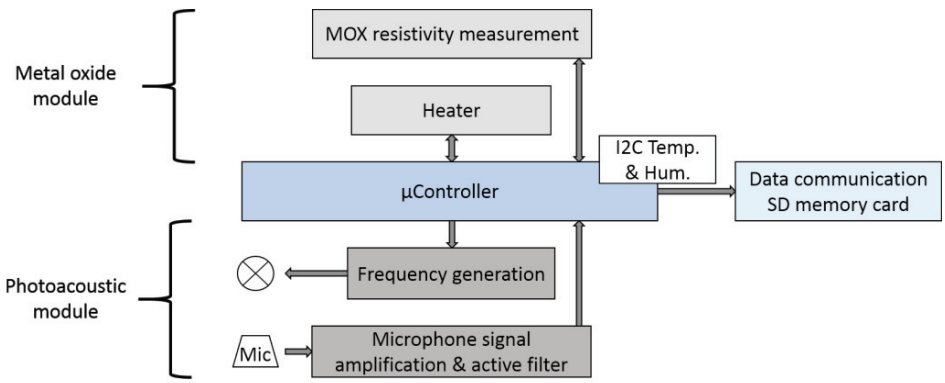

Fig. 1. The sensor system comprises three basic modules, i.e. the metal oxide module for the determination of the H_2S content, the photoacoustic module to measure the CO_2 and CH_4 content, and a commercially available I^2C sensor to determine ambient temperature and humidity. All data are stored using a SD memory card.

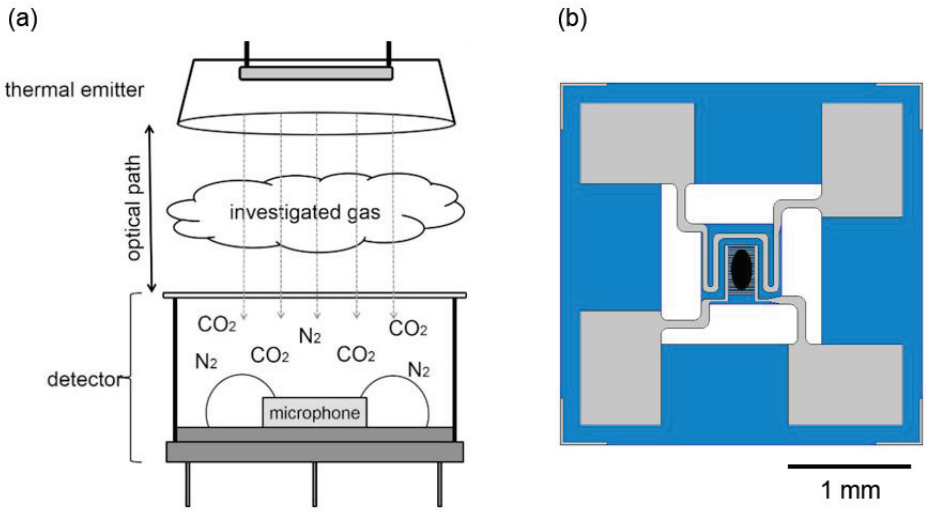

Fig. 2. (a) A schematic drawing of the photoacoustic module using CO_2 as exemplary target gas. The distance between emitter and detector acts a measurement path and the increasing concentration of the target gas results in a lowering of the detected signal. (b) A micromachined metal oxide device consisting of a heating element and an interdigitated electrode structure (gray), carrying the functional CuO layer (black) is used to determine the H_2S concentration.

3. Results

The system has been characterized in a custom built laboratory apparatus capable of simulating real-world environments to highlight the system's capabilities [11]. To this end, the system's reaction towards 0 % – 50% of CH4 and CO_2 has been quantified for different humidity levels, respectively. Furthermore, the reaction towards H2S has been explored in the range of 0 – 2 ppm. The results are depicted in Figure 3-5.

Due to the strong absorption band around 4.2 µm the response of the CO_2-module saturates from 40% carbon dioxide concentration, which is, however, well above the typically occurring 30% CO_2 content in biogas reactors. The gas sensitive results presented in Figure 3 show the sensor response from 5% - 50% CO_2 concentration in dry nitrogen (N_2). The sensor response is the ratio of the sensor signal in dry N_2 and varying levels of CO_2 which is stored in N_2.

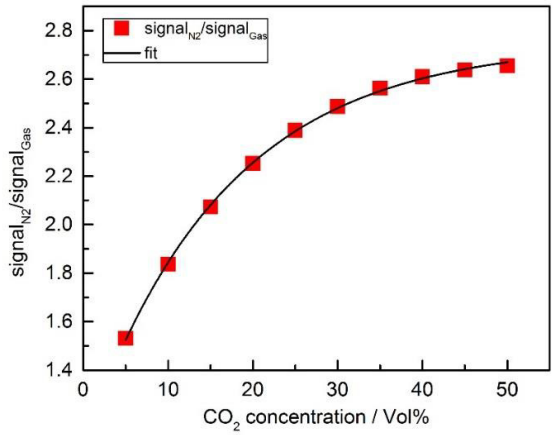

Fig. 3. (a) Sensor response towards varying levels of CO_2 in dry nitrogen.

Figure 4 depicts the corresponding measurements for the CH_4 module. Since the absorption of methane is weaker no saturation is detected implying the suitability of the sensor to cover the complete range between 0% - 100% CH_4.

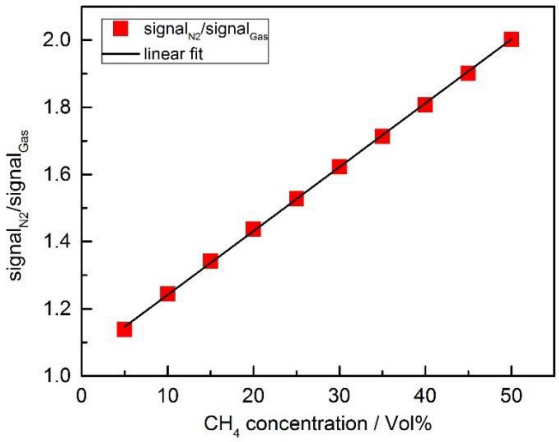

Fig. 4. Sensor response to varying levels of methane. The response is highly linear in the complete measurement range.

To determine the H_2S concentration a novel scheme employing CuO as gas sensitive layer has been implemented. It relies on the measurement of the H_2S-dependent so-called percolation time necessary to establish a conducting path between two electrodes via the formation of CuS cluster according to the reaction:

$$H_2S_{(g)} + CuO \rightarrow H_2O_{(g)} + CuS \quad . \tag{1}$$

Figure 5 shows the percolation time for an operating temperature of 150°C and an atmosphere consisting of 2% oxygen, 1.5 ppm H_2S and nitrogen. The percolation time is statistically distributed around the mean value. An increase of the H_2S concentration leads to shorter percolation times.

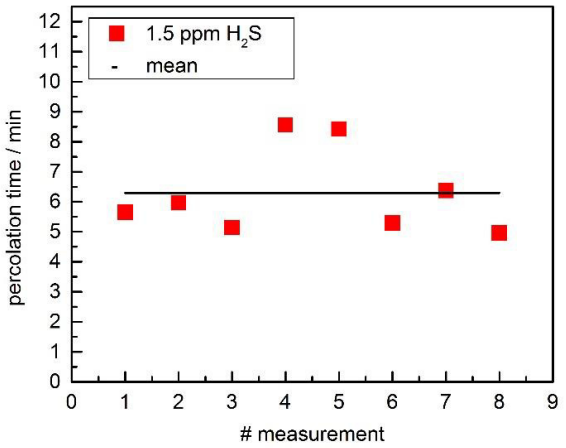

Fig. 5. Percolation times for a concentration of 1.5 ppm H2S in a dry atmosphere consisting of 98% N_2 and 2 % O_2.

4. Conclusion

In this contribution we have presented a novel gas measurement system capable of determining the concentrations of the most important constituents of the gas atmosphere inside a biogas reactor, i.e. methane, carbon dioxide and hydrogen sulfide. The system is composed of low-cost components only and may be fully integrated into a micro-machined system. They constitute a viable and more powerful alternative to currently employed approaches, namely NDIR technology for CO_2 and CH_4 and electrochemical cells for H_2S.

Acknowledgements

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